

XAFS/XANES studies of plutonium-loaded sodalite/glass waste forms

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Introduction

Sodalite/glass composite waste forms are being developed at Argonne National Laboratory (ANL) for disposal of radioactive fission elements in salt form from the electrometallurgical treatment of spent EBR-II nuclear reactor fuel [1, 2]. The salt waste from the electrometallurgical process consists primarily of a LiCl/KCl eutectic salt loaded with various other fission-product chloride salts. In addition, this salt contains up to 2 mol % actinide chlorides, namely uranium, plutonium, and neptunium chlorides. The salt from the treatment process is sorbed by zeolite 4A, which has an aluminosilicate cage structure of nominal composition $\text{Na}_{12}(\text{AlSiO}_4)_{12}$ and is known for its ability to contain or "occlude" other species within the cage structure. The zeolite 4A, with its occluded fission-element salts, is mixed with glass and heated to high temperatures and pressures to convert the zeolite to a more thermodynamically stable sodalite form and to consolidate the waste form. Primary considerations in this process are (1) questions of reactivity of the various salts with the zeolite structure as raised by thermodynamic calculations and (2) the fate of the fission elements in the resulting waste form. The objective of this work was to determine the fate of plutonium in this waste form via x-ray absorption fine structure (XAFS) and x-ray absorption near-edge structure (XANES) synchrotron techniques [3,4]. Other techniques, such as tunneling electron microscopy (TEM), can show crystal structure in great detail but do not have the ability to see the plutonium within the sodalite cage structure. The XAFS technique provides a unique means of determining the local environment of the plutonium where other techniques are effectively blind.

Methods and Materials

Sample preparation

The samples consist of zeolite 4A blended with sufficient LiCl/KCl/PuCl₃ salt such that the zeolite is loaded to 3.8 chlorides per unit zeolite cell on average. This blended material is then mixed with sufficient glass powder to achieve a mixture that is 25 weight percent glass. The mixture is then pressed in a graphite die to 6600 psi and a final temperature of 750 degrees Celsius and allowed to cool. More specific detail in this preparation can be found in [5].

Small bulk pieces of this material were then mounted within a styrene epoxy and covered with Kapton for containment. In the simulated fission salt case, half of the bulk ceramic pieces were kept in an anhydrous state, and the remainder were allowed to absorb water from the atmosphere (~50% relative humidity) for 96 hours prior to sample mounting to observe any environmental water absorption effects upon

the plutonium. The eutectic salt cases were kept in an anhydrous state.

XAFS/XANES standards

Representative plutonium-containing standards were used in the course of this investigation. Each standard was prepared [4] to cover a particular plutonium oxidation state. The following standards were used: Pu(III)F₃, Pu(IV)O₂, NaPu(V)O₂CO₃, and Ba₃Pu(VI)O₆. The standards are all fine powders dispersed on Kapton tape and encapsulated in a styrene matrix. Since the actinide L edges are all at fairly high energy (>15 keV), the encapsulation matrix is essentially transparent.

Results

XANES data were acquired for the PuCl₃/LiCl/KCl and found to be a good match to the Pu⁺⁴ oxidation state [4].

XAFS data were acquired for all of the cases (Pu salt with and without simulated fission elements and wet versus dry sample) and were found to be an excellent match to the PuO₂ standard. Figure 1 is a plot of the fit of the isolated first- and second-shell data from one of the representative unknowns as compared to the plutonium dioxide standard. As one can see, the agreement between the two cases is as good as can possibly be expected if the unknown sample contained plutonium only in the dioxide form. Other chemical species were considered using crystallographic data even with the essentially perfect match to the PuO₂ standard: PuO, Pu₂O₃, PuOCl, PuCl₃, K₂PuCl₅, and K₂PuCl₆. The first two species [6, 7] yielded Pu-Pu distances that were completely discordant with the experimental data. PuOCl failed to yield a fit [6] that would reconcile the experimental radial shell amplitudes with the theoretical fit. The plutonium chloride [8] and potassium plutonium chloride [9–11] species also were a poor match to the experimental Pu-Pu distances.

Discussion

All cases considered in this experiment generated essentially identical results. Thermodynamic calculations of the expected products of reaction generated by mixing these salts with zeolite at elevated temperature indicate the possible formation of oxides, oxychlorides, and perhaps chlorides. The XAFS/XANES results rule out the significant formation of the latter two cases.

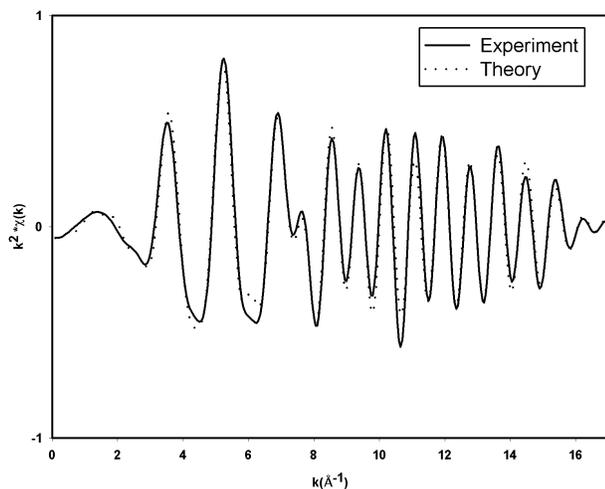


Figure 1: Plot (fitted) of the isolated first- and second-shell data from one of the representative unknowns as compared to the plutonium dioxide standard.

Comparison of the Fourier-transformed (FT) data for the simulated fission product element salt cases, both wet and dry, against the PuO_2 standard indicated an average particle size compatible with a central plutonium surrounded, on average, by seven plutonium nearest neighbors. A nominally filled second shell consists of 12 plutonium atoms, which would give rise to 5.5 plutonium nearest neighbors. This arrangement would give a particle size of about 13 Å, given the known Pu-Pu distance of 3.82 Å and the oxygen atoms that must surround the plutonium atoms to give charge balance. Given the previously discussed known sodalite cage free diameter of 6.6 Å, the plutonium oxide appears to be completely outside of the sodalite cage. Similar comparison of the plutonium-loaded eutectic-salt-only case yielded amplitudes that put the average crystallite size larger than that which could be determined by the XAFS technique. Comparing the PuO_2 lines determined crystallographically put the particulate size at 20 nm or possibly greater.

In summary, utilization of the XAFS/XANES techniques determined that 1) plutonium is present in these samples completely as plutonium (IV) dioxide within the limits of detection; 2) no differences were observed between the different types of samples except for particulate size; and 3) in all cases, the plutonium dioxide particulate size was large enough to preclude incorporation into the final sodalite lattice.

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